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# Solvatochromic Behavior of Donor−Acceptor-Polyenes: Dimethylamino-cyano-diphenylbutadiene

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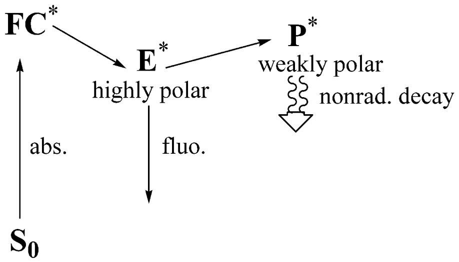
4-(Dimethylamino)-4′-cyano-1,4-diphenylbutadiene (DCB) and 4-(dimethylamino)-2,6-dimethyl-4′-cyano-1,4-diphenylbutadiene (DMDCB) have been characterized spectroscopically. Quantum chemical calculations were performed for comparison. Solvatochromic shifts of the fluorescence were strong and showed a linear dependence on the solvent polarity parameters, whereas shifts in the absorption spectra are very weak only correlate better with the polarizability of the solvents. Excited state dipole moments derived from fluorescence using the Onsager model are very large and similar for both compounds. It is concluded that a strongly allowed and highly dipolar $\pi, \pi^*$ state is the lowest excited state in polar solvents. The strong difference in absorption and fluorescence solvatochromic slopes suggests that the simple Onsager model with a point dipole approximation is not sufficient here.

## 1. Introduction

The photophysical and solvatochromic properties of push−pull stilbenes, i.e., stilbenes substituted with a donor and an acceptor group in conjugated positions, have attracted old[1,2] and recent interest.[3−14] In view of their structure similar to typical fluorescent probes and imaging dyes[15] used in cellular calcium sensing and dyes used in the visualization of membrane nerve potentials,[16] it is of interest to get a deeper understanding of the underlying photophysical mechanisms. Several steps in this direction have been reviewed recently,[17,18] and we want to focus here on the case of diphenylbutadienes.

The parent compound *trans*-stilbene is well-known for its adiabatic photoreaction leading to the ground state by population of the so-called "phantom-singlet" state P* reachable by double-bond twisting. This twisted conformation corresponds to a maximum on the ground state surface to which it is strongly coupled in this region of phase-space (possibly by a conical intersection),[3,19] and this twisting pathway thus provides an effective ultrafast deactivation funnel.[20,21] In push−pull stilbenes, an additional photochemical pathway is open in principle, which involves the twisting of one of the single bonds adjacent to the central double bond and leads to a relaxed intramolecular charge transfer excited state A*, which is characterized by a very high dipole moment, even larger than that of the relaxed planar state E*, which has also a high dipole moment for push−pull stilbenes.[4,5,8,9] The dipole moment of the P* state (see Scheme 1), on the other hand, is expected to be small in push−pull stilbenes but large in the parent stilbene.[6,21] Strong evidence for a decisive role of the single bond twisting comes from the study of bridged model compounds of dimethylamino-cyano-stilbene (DCS).[4,6,14] However, it remains unclear whether the relaxed A* state has a twisted intramolecular charge transfer (TICT)[22] nature because there is no significant reduction of the radiative rate ($k_f$) with A* formation[4,5] whereas a reduction of $k_f$ is typically observed for the involvement of a TICT state. Also for dimethylamino-nitro-stilbene (DNS) and other derivatives with electron donating and electron accepting substituents the quantum yields of fluorescence, internal conversion and intersystem crossing are sensitive functions of solvent polarity.[23−25] Not only the exit from the $S_1$ energy surface but also the character of the primary excited state depends on the solvent. When the polarity is increased, the first absorption band and especially the fluorescence spectrum of DNS are red shifted[25] resulting in an increased Stokes shift. The latter effect suggests a large increase of the dipole moment from the ground state to the excited state. In solvatochromic dipole determination it is often assumed that the excited state dipole moment is independent of the solvent polarity and identical for the Franck−Condon (FC) and the relaxed excited state.[26] However, in DNS the situation is clearly more complicated. Instead of a monotonic red shift of the absorption band with increasing solvent polarity, a nonmonotonic behavior is observed.[27] This indicates that the dipole moment of the FC excited state, and therefore the charge transfer character, depends on the surrounding.

**SCHEME 1: Mechanistic Scheme for the Photophysical and Photochemical Deactivation of the Excited State of Stilbenoids[a]**



[a] The possible population of an A* state has been disproved for the compounds studied here; see the Introduction.

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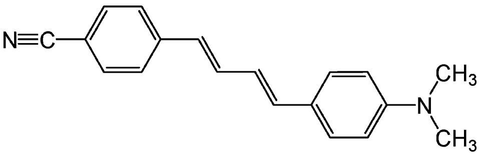
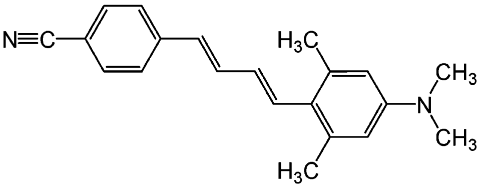
**CHART 1: Structures of the Molecules Investigated**



**DCB**



**DMDCB**

We have recently studied the possible involvement of a TICT state for the case of dimethylamino-cyano-diphenylbutadiene (DCB) by comparing the photophysical properties of this compound with those of a twisted model compound, the sterically hindered dimethylated derivative DMDCB (see Chart 1). There was no evidence for the involvement of a TICT (A*) state for this pair of compounds.[28] The main focus of the present paper is on the solvatochromic comparison of these two compounds. The strongly different solvatochromic slopes for absorption and fluorescence are not compatible with the usual assumption of the same state for absorption and emission or with the validity of a point dipole in a solvent continuum Onsager model.[29]

## 2. Experimental Section

**2.1. Materials.** The preparation and chemical identification of the donor−acceptor 1,4-diphenylbutadienes, DCB and DMDCB, was done according to known literature.[30] The solvents for the spectroscopic measurements: *n*-hexane, dipentyl ether (POP), diethyl ether (EOE), dibutyl ether (BOB), tetrahydrofuran (THF), ethanol (EtOH), acetonitrile (ACN), 1-chlorobutane, dichlorobutane, tetrachloromethane, and pyridine were Uvasol grade from Merck and 1,2-dichloroethane and chlorobenzene were of spectroscopic grade from Aldrich and were tested before use. The solutions were prepared to optical densities of 0.09−0.10 for steady state. The solutions of DCB and DMDCB were prepared under red light a care was taken to verify that photochemistry during the experiments was negligible. Neither absorption nor fluorescence spectra were affected during the measurement.

**2.2. Spectroscopy.** Absorption spectra were recorded on an AT1 Unicam spectrometer UV4, and the steady state fluorescence spectra were recorded with a SLM Aminco-Bowman AB2 spectrofluorometer. The fluorescence excitation and emission spectra were corrected for instrumental sensitivity. The emission correction curves were created using a calibrated tungsten lamp from SLM instruments, and the excitation correction curves were created using the excitation spectrum of a quantum counter solution of Basic Blue 3.[31]

**2.3. Quantum Chemical Calculations.** All quantum chemical calculations were performed using the AM1 method within the AMPAC program package.[32] Full geometry optimization for the ground state structure of the species under consideration was performed. For twisted geometries, the corresponding dihedral angle was fixed, and all the remaining variables were fully optimized.

FC excited states were calculated for fixed ground state geometries as indicated using extensive configuration interaction, CI (ca. 400 singly, doubly and higher excited configurations). The relaxed $S_1$ state was calculated by full geometry optimization including the same CI.

To check the reliability of the AM1 method, we compared our calculation on DCS using the AM1 method to a more sophisticated computation (ab initio CASSCF method) as given in ref.[33] Both methods yield consistent results regarding ground and excited state dipole moments and oscillator strength. Also, the excitation energy to $S_1$, 3.27 eV with the AM1 method and 3.51 eV with the ab initio calculation (including MRMP2 correction)[33] is close to the experimental value (3.35 eV).

## 3. Results

**3.1. Absorption and Emission Solvatochromy.** Figure 1 shows room temperature absorption and fluorescence spectra of DCB and DMDCB, respectively in solvents of different polarity. The absorption maxima show only a very slight red shift with increasing solvent polarity, normally interpreted as indicating that the ground state and the FC excited state have similar dipole moments, whereas the fluorescence spectra show a strong solvatochromic red shift indicative of a very high excited state dipole moment as compared to that of the FC ground state. The detailed absorption and emission maxima as well as Stokes shifts and half bandwidths are collected in Table 1. The details of quantum yield, lifetime, radiative decay and nonradiative decay values can be found in ref. 28.

**3.2. Excited State Dipole Moments.** The solvent-induced spectral shifts in absorption are close to zero, except for the solvents THF, 1-chlorobutane, dichloromethane, 1,2-dichloroethane, chlorobenzene, tetrachloromethane and pyridine, which deviate from the other solvents due to their higher refractive indices. According to the solvatochromic equations of Liptay[34] (eqs 1 and 2), the solvatochromic absorption can be calculated

$$\tilde{\nu}_{\mathrm{abs}} = \tilde{\nu}^{0}_{\mathrm{abs}} - \frac{1}{4\pi\epsilon_0}\frac{2}{hc\chi\alpha^3}\left[\mu_g(\mu_{\mathrm{e}}^{\mathrm{FC}} - \mu_{\mathrm{g}})\frac{\epsilon - 1}{2\epsilon + 2} + \frac{1}{2}(\mu_{\mathrm{e}}^{\mathrm{FC}} - \mu_{\mathrm{g}})^2\frac{n^2 - 1}{n^2 + 2}\right] \quad (1)$$

$$\tilde{\nu}_{\mathrm{flu}} = \tilde{\nu}^{0}_{\mathrm{flu}} - \frac{1}{4\pi\epsilon_0}\frac{2}{hc\chi\alpha^3}\left[\mu_{\mathrm{e}}(\mu_{\mathrm{e}} - \mu_{\mathrm{g}}^{\mathrm{FC}})\frac{\epsilon - 1}{2\epsilon + 2} - \frac{1}{2}(\mu_{\mathrm{e}}^{\mathrm{FC}} - \mu_{\mathrm{g}})^2\frac{n^2 - 1}{n^2 + 2}\right] \quad (2)$$

according to eq 3, where the slope is proportional to $\mu_{\mathrm{g}}(\mu_{\mathrm{e}}^{\mathrm{FC}} - \mu_{\mathrm{g}})$, with $\mu_{\mathrm{g}}$ being the dipole moment of the ground state, $\mu_{\mathrm{e}}^{\mathrm{FC}}$ that of the FC state reached in absorption and $\Delta f$ the polarity parameter used by Lippert.[35] For a zero solvatochromic slope

$$\nu_{\mathrm{abs}} = -\frac{1}{4\pi\epsilon_0}\mu_{\mathrm{g}}(\mu_{\mathrm{e}}^{\mathrm{FC}} - \mu_{\mathrm{g}})\Delta f + \text{constant} \quad (3)$$

$$\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$$

of a dipolar molecule, the ground and FC excited state dipole moments must be roughly equal and can therefore be approximated by the dipole moments obtained in the ground state calculations, i.e., ca. 6.2 D for DCB, and ca. 5.6 D for DMDCB (Table 2).

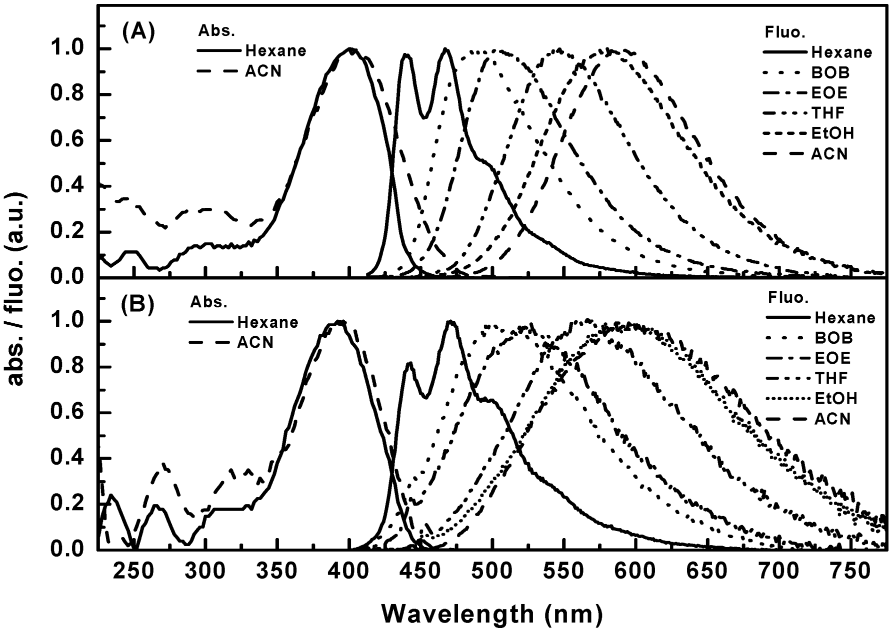


**Figure 1.** Normalized absorption and fluorescence spectra of (A) DCB and (B) DMDCB in solvents of different polarity. The abbreviations for the solvents are given in the materials section.

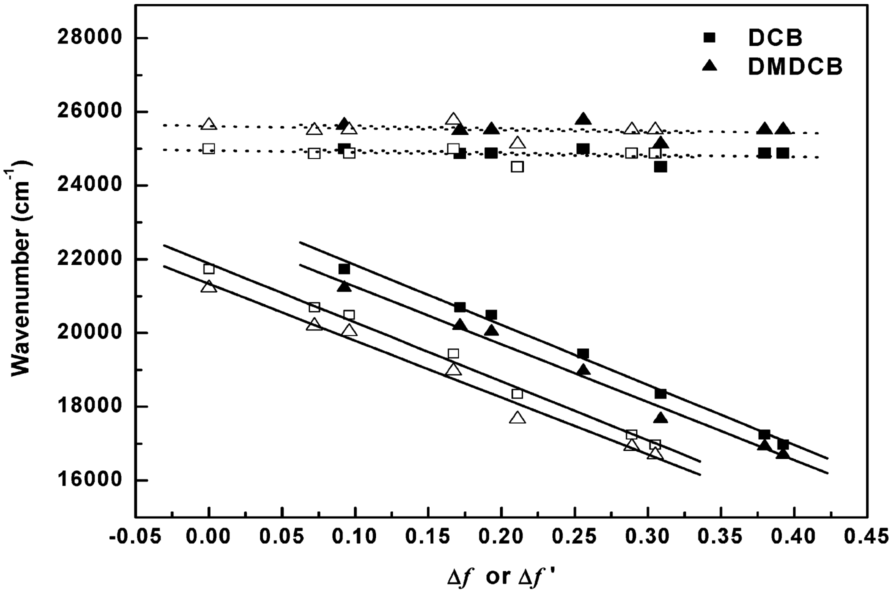


**Figure 2.** Absorption (···) and fluorescence maxima (—) $\tilde{\nu}^{max}$ or DCB (■) and DMDCB (▲) versus $\Delta f$ (open symbols) and $\Delta f'$ (filled symbols) in different solvents.

The excited state dipole moments $\mu_e$ of DCB and DMDCB are quantified in Figure 2 by a solvatochromic plot of the fluorescence according to the Mataga equation (eq 4),[36] where

$$\tilde{\nu}_{flu} = -\frac{1}{4\pi\epsilon_0}\frac{2}{hc\alpha^3}\mu_e(\mu_e - \mu_g^{FC})\Delta f' + \text{constant} \qquad (4)$$

$$\Delta f' = [(\epsilon - 1)/(2\epsilon + 1)] - 0.5[(n^2 - 1)/(2n^2 + 1)]$$

$\mu_g^{FC}$ and $\mu_e$ are the dipole moments of the molecule in the FC ground and the relaxed excited states, respectively, and where $h$ is the Planck's constant and $c$ is the speed of light and $\epsilon_0$ is the permittivity of the vacuum. $\tilde{\nu}_{flu}$ is the fluorescence band maximum expressed in cm$^{-1}$. The Onsager cavity radius $a$ has been approximated, following Lippert's suggestion[35] for non-spherical molecules, as 40% of the longest axis of the compound. $\Delta f'$ is Mataga's polarity-polarizability parameter[36] of the solvent depending on the dielectric constant $\epsilon$ and refractive index $n$ of the solvent.

As can be seen in Figure 2, the values of $\tilde{\nu}_{flu}$ decrease linearly with increasing solvent polarity $\Delta f'$ and a good regression analysis is obtained. This figure also shows that the slope does not depend on which of the two solvent polarity parameters is used in the analysis, $\Delta f$ or $\Delta f'$.

Table 2 presents the excited state dipole moments as obtained from the absorption and emission solvatochromic slopes and using the calculated $\mu_g$ values as obtained from the AM1 semiempirical calculations.

The absorption and fluorescence results for the determination of the excited state dipole moment disagree strongly. Although the fluorescence solvatochromy leads to a large excited state dipole moment (around 19 D), the vanishing absorption solvatochromy points to a relatively small dipole moment of the FC

**TABLE 1: Spectral Characteristics of DCB and DMDCB in Solvents of Increasing Polarity As Characterized by Their Dielectric Constant $\epsilon$ and Refractive Index $n$**

| compound | solvent | $\epsilon$ | $n$ | $\lambda_A$ (nm) | $\lambda_F$ (nm)[a] | $\Delta\tilde{\nu}_{\mathrm{Stokes}}$ (cm$^{-1}$)[a] | Fwhm (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| DCB | *n*-hexane | 1.88 | 1.375 | 400 | 440, $\underline{460}$ | 2273, $\underline{3261}$ | 3162 |
| | BOB | 3.08 | 1.399 | 402 | 488 | 4384 | 3268 |
| | EOE | 4.34 | 1.352 | 400 | 509 | 5354 | 3227 |
| | THF | 7.58 | 1.405 | 408 | 545 | 6160 | 3296 |
| | EtOH | 24.3 | 1.361 | 402 | 580 | 7635 | 3376 |
| | ACN | 37.5 | 1.344 | 402 | 589 | 7898 | 3563 |
| DMDCB | *n*-hexane | 1.88 | 1.375 | 390 | 442, $\underline{471}$ | 3017, $\underline{4150}$ | 3789 |
| | BOB | 3.08 | 1.399 | 392 | 499 | 5470 | 4107 |
| | EOE | 4.34 | 1.352 | 388 | 527 | 6798 | 4008 |
| | THF | 7.58 | 1.405 | 398 | 566 | 7458 | 4184 |
| | EtOH | 24.3 | 1.361 | 392 | 591 | 8721 | 4639 |
| | ACN | 37.5 | 1.344 | 392 | 599 | 8947 | 4738 |

[a] In case of double maxima, the main one is underlined and used for the solvatochromic plot.

**TABLE 2: Solvatochromic Slopes of Fluorescence and Absorption and Derived Dipole Moment Values for Relaxed and Franck Condon Excited States (Using Eqs 3 and 4)**

| compound | $a$[a] (Å) | $\mu_g$[b] (D) | fluorescence slope (cm$^{-1}$) (vs Mataga) | absorption slope (cm$^{-1}$) (vs Lippert) | $\mu_e$ (D) | $\mu_e^{\mathrm{FC}}$(D) |
|---|---|---|---|---|---|---|
| DCB | 7.3 | 6.2 | −16271 | −573 | 19.3 | 7.9 |
| DMDCB | 7.3 | 5.6 | −15678 | −522 | 18.7 | 7.1 |

[a] The Onsager cavity radius has been estimated from 40% of the long molecular axis. [b] $\mu_g$ calculations were performed using the AM1 method.

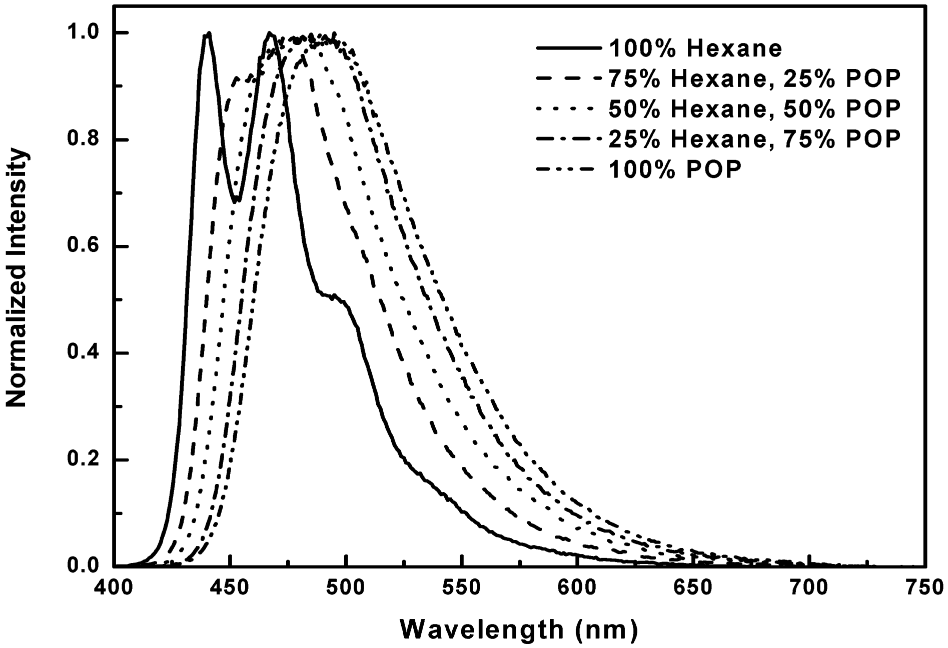


**Figure 3.** Formalized fluorescence spectra of DCB in the solvent mixture *n*-hexane with dipentyl ether (POP).

excited state (around 7−8 D). The discrepancy between absorption and emission solvatochromy in donor−acceptor substituted diphenyl butadiene DCB can be compared to the corresponding behavior of donor−acceptor substituted stilbenes, where a similar discrepancy has been reported.[12] Various possible explanations for this discrepancy are treated in the discussion section.

We performed an additional experiment aimed at investigating a further possible explanation, namely enhancement of the fluorescence solvatochromic slope through a change of the relative weight of the FC factors with solvent polarity, whereas the individual vibronic bands stay at the same spectral position instead of exhibiting a continuous red shift. The spectra in mixed hexane−dipentyl ether solvent (Figure 3) show a clear continuous red shift of the vibronically structured emission features seen in hexane and exclude this possibility and point to a true solvatochromic red shift of the fluorescence.

**3.3. Theoretical Calculations**. To get additional information that might help to discuss the discrepancy of absorption and emission solvatochromy, we performed a geometry optimization of DCB in the excited state. In Table 3, which is discussed in more detail below, we can see that after geometry relaxation, the oscillator strength becomes higher, but the dipole moment remains the same or even shows some decrease. Excited state geometrical relaxation can therefore also be ruled out as being the source of the strong solvatochromic enhancement in emission. As expected, the bond lengths were changed by the relaxation, loosing their regular aromatic structure and favoring the quinoid structure and leading to a near-equalization of double and single bonds as seen in Figure 4.

**TABLE 3: AM1-CI Calculations for the Electronic Transitions of DCB at α = 0° for (a) the Relaxed Ground State and (b) the Relaxed Excited State and (c) Comparison to a ZINDO/S-CI Calculation for the Relaxed Ground State**

| state | $\Delta E$ (eV) | $f$ | CI analysis | $\mu$ (Debye) |
|---|---|---|---|---|
| | | (a) Ground State Geometry | | |
| $S_0$ | 0 | | | 6.84 |
| $S_1$ | 3.39<br>(exp: 3.1) | 1.22 | 72% (52−53)<br>12% (52−54) | 16.9 |
| | | (B) Relaxed (Geometry Optimized) Excited State | | |
| $S_0$ | 0 | | | 6.84 |
| $S_1$ | 2.90 | 1.42 | 84% (52−53)<br>6% (52−54) | 16.1 |
| | | (c) ZINDO/S Calculation for the Ground State Geometry | | |
| $S_1$ | 3.55 | 1.31 | 96% (52−53)<br>18% (52−54)<br>18% (51−54) | |

From these results, the wave function for ground and excited states can be given by eqs 5 and 6.

$$\Psi_{S0} = a_0\psi_{Ar} + b_0\psi_Q \tag{5}$$

$$\Psi_{S1} = a_1\psi_{Ar} + b_1\psi_Q \tag{6}$$

$$\text{with} \quad a_1 \ll a_0 \quad \text{and} \quad b_1 \gg b_0$$

The experimental solvatochromic results can be interpreted in two ways:

Model 1: We assume the validity of the Onsager theory (solvent reaction field as answer to a point dipole changing from ground to excited state) and Model 2: We allow for a breakdown of this assumption.

If we use Model 1, the small solvatochromy in absorption indicates a similar wave function for $S_0$ and $S_1^{FC}$, ($\Psi_{FC*} \approx \Psi_{S0}$) because of the low dipole moment in both cases. But the fluorescence solvatochromy indicates a strong change of the wave function in the relaxed excited state E* ($\Psi_{E*} \approx \Psi_{S1}$) with a large increase of quinoid contributions resulting in a large dipole moment as shown in eq 6.

From our calculations on stilbenoids,[37,38] it is known that the change of the contributions of $\psi_{Ar}$ and $\psi_Q$ is linked with a shortening and lengthening of single and double bonds, and the magnitude of changes depends on the relative donor−acceptor strength. DCS has a relatively weak donor−acceptor strength $\Delta E_{DA}$,[39] and the bond-length and photophysical changes from FC* to E* are expected to be sizable.[38] For larger values of $\Delta E_{DA}$, these changes become smaller and vanish at a certain point, the so-called “cyanine-limit”.[37,38] From the combination of the results presented here with the above model we can therefore derive the bond length changes as a convenient parameter to quantify the relation of a given polyenic/polymethinic dye with respect to the cyanine limit. Ab initio quantum chemical calculations with optimization in the excited state have indeed verified that acceptor-disturbed polyenes, i.e., models for the visual chromophore retinal Schiff base, first relax by bond length changes and only then by twisting of bonds in the excited state.[40] It could be thought that this initial bond length relaxation might yield a basis for the large changes of the wave function between FC and relaxed $S_1$ within the model 1.

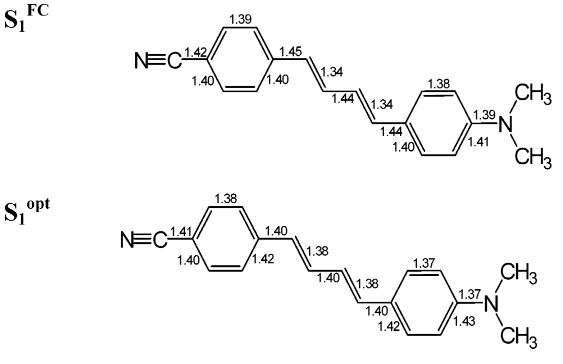


**Figure 4.** Bond lengths of the optimized geometrical structure of the ground state (and Franck−Condon excited state) and the relaxed $S_1$ state of DCB. Large structural in-plane rearrangements occur in the excited state relaxation.

**SCHEME 2: Valence Bond Resonance Structures and Definition of Twist Angles for DCB**

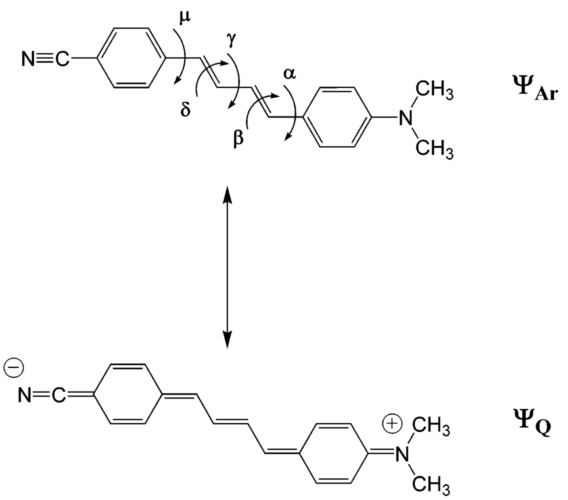


**TABLE 4: AM1 Calculations for the Electronic Transitions of DMDCB at α = 0° and at the Equilibrium Twist Angle α = 45°**

| state | $\Delta E$ (eV) | $f$ | CI analysis | $\mu$ (Debye) |
|---|---|---|---|---|
| | | α = 0° | | |
| $S_0$ | 0 | | | 6.68 |
| $S_1$ | 3.28 | 1.20 | 70% (58−59)<br>12% (58−60) | 15.2 |
| $S_2$ | 3.83 | 0.0006 | 72% (58−62)<br>10% (56−60) | 8.93 |
| $S_3$ | 4.33 | 0.0007 | 46% (58−60)<br>16% (57−59) | 16.3 |
| $S_4$ | 4.44 | 0.332 | 16% (57−59)<br>12% (58−60) | 15.7 |
| $S_5$ | 4.75 | 0.006 | 40% (57−60)<br>6% (55−61) | 18.8 |
| | | α = 45° | | |
| $S_0$ | 0 | | | 5.57 |
| $S_1$ | 3.61<br>(exp: 3.2) | 1.08 | 68% (58−59)<br>14% (58−60) | 15.51 |
| $S_2$ | 4.19 | 0.0007 | 70% (58−62)<br>6% (56−59) | 8.86 |
| $S_3$ | 4.43 | 0.0168 | 44% (57−59)<br>32% (58−60) | 10.07 |
| $S_4$ | 4.57 | 0.0004 | 48% (55−59)<br>14% (58−61) | 15.88 |
| $S_5$ | 5.04 | 0.625 | 28% (58−60)<br>7% (57−59) | 18.51 |

To obtain information on this, we performed the calculations reported in Table 3 and Figure 4 with the aim to quantify the wave function changes upon $S_1$ relaxation. Although there is a considerable geometrical relaxation from the FC to the relaxed excited state (Figure 4), the dipole moment does not increase but decreases slightly (Table 3); i.e., a strong increase of the dipole moment brought about by the relaxation is not supported by these calculations.

**TABLE 5: Ground State Geometry and the Electronic Transition Characteristics [Dielectric Energy (eV), Heat of Formation (eV), Dipole Moment (Debye), Electron Density on the Amino Nitrogen Atom, and Oscillator Strength] in Vacuum, Hexane and Acetonitrile Calculated by AM1/COSMO**

| solvent | $\epsilon/n$ | dielectric energy (eV) | $S_0$ $\Delta H_f$ (eV)/$\mu_0$/$q_N$ | $S_1$ $\Delta E$ (eV)/$\mu_1$/$q_N$/$f$ | $S_2$ $\Delta E$ (eV)/$\mu_2$/$q_N$/$f$ |
|---|---|---|---|---|---|
| | | | (a) DCS | | |
| vacuum | | | 3.77/6.26/5.25 | 3.59/13.8/5.12/0.905 | 4.13/8.81/5.07/0.023 |
| hexane | 1.88/1.375 | −0.21 | 3.56/6.83/5.26 | 3.53/14.2/5.12/0.883 | 4.07/9.48/5.08/0.021 |
| acetonitrile | 37.5/1.344 | −0.71 | 3.19/7.97/5.27 | 3.51/15.6/5.11/0.884 | 4.03/10.7/5.06/0.019 |
| | | | (b) DCB | | |
| vacuum | | | 4.38/6.84/5.25 | 3.39/16.9/5.15/1.221 | 4.14/9.48/5.05/0.001 |
| hexane | 1.88/1.375 | −0.22 | 4.18/7.24/5.26 | 3.36/17.9/5.16/1.198 | 4.12/9.65/5.06/0.055 |
| acetonitrile | 37.5/1.344 | −0.77 | 3.78/8.33/5.27 | 3.34/18.8/5.15/1.199 | 4.11/10.7/5.05/0.004 |

We also did some additional AM1 calculations to obtain some information about the conformational effects introduced by the t*wo*-methyl substituents and on their effects on the absorption spectra. DCB is near to planar in the ground state, whereas the dimethylanilino moiety is twisted by about 45° in DMDCB, due to the sterical hindrance of the t*wo*-methyl groups. This causes a slight blue shift of the spectra as shown below.

The ground state rotational barriers show an alternation along the bonds α to $\mu$ (for definition see Scheme 2) with very small and very large barriers for essential single and double bonds. This alternation is lost or even reversed in the excited state. We can conclude that in the excited state, the electronic structure changes in a way that nearly equalizes the bond orders with the results that all bonds possess similar rotational barriers. This is consistent with the result of the excited state optimization (Figure 4) where double and single bonds nearly become equalized.

The calculated energies and oscillator strengths and principal configurations for the lowest five singlet transitions are calculated for the relaxed ground state geometry and represent the absorption spectrum. They are listed in Tables 3 and 4. The experimental energies are only 0.3−0.4 eV overestimated by

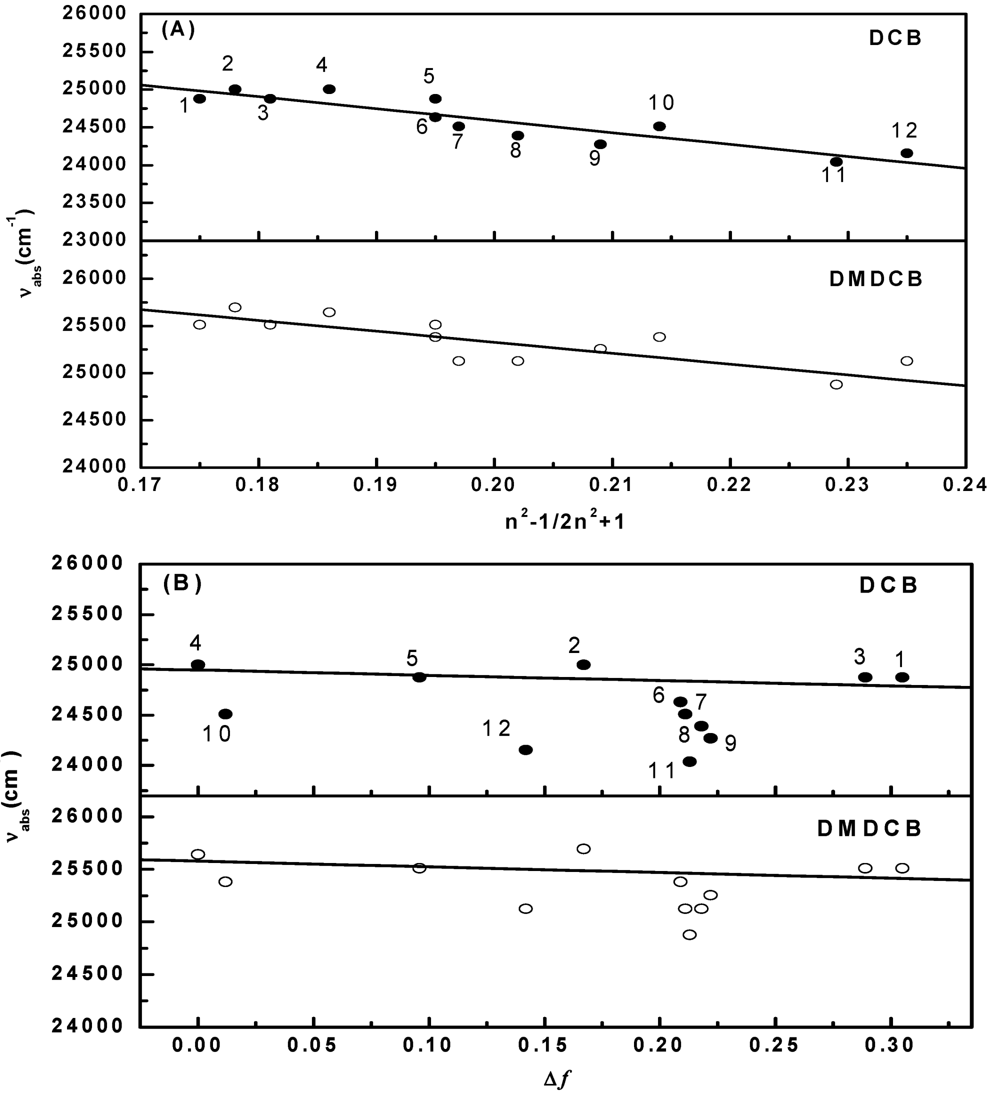


**Figure 5.** Plot of absorption maxima of DCB and DMDCB in various solvents [(1) ACN, (2) EOE, (3) EtOH, (4) *n*-hexane, (5) BOB, (6) 1-chlorobutane, (7) THF, (8) dichloromethane, (9) 1,2-dichloroethane, (10) tetrachloromethane, (11) pyridine, (12) chlorobenzene] versus (A) the solvent polarizability given by ($n^2$-1)/(2$n^2$+1); (B) the solvent polarity parameters, Δ*f*.

AM1 and ZINDO, showing that both methods are similarly reliable in predicting absorption spectra, and the blue shift due to the twist angle in DMDCB is correctly predicted. The main absorption band corresponds to an allowed transition to $S_1$ mainly involving the frontier orbitals.

Table 5 shows the results of COSMO calculations including the effect of the solvent into the calculation procedure of the wave function. These calculations therefore contain the polarizability response of the solute to the polarity of the solvent. The results show that the dipole moment is already large in a vacuum and does not increase strongly by introducing a polar solvent. The results are discussed in more detail below.

Figure 5 shows a comparison of different solvatochromic treatments for the absorption solvatochromy. It can be seen that the solvatochromic shift of the absorption maxima does not correlate well with the solvent polarity parameter $\Delta f$ but that it correlates much better with the solvent polarizability $f(n^2)$ at least for the solvents where the refractive index changes strongly. Such a behavior has also been observed for donor−acceptor stilbene by Rechthaler et al.[12]

## 4. Discussion

**4.1. Discrepancy of the Absorption and Emission Solvatochromy.** The results of the dipole moment analysis in Table 2 indicate a very large difference between the FC and the relaxed excited state dipole moment. The FC dipole moment seems to be anomalously small as compared to the dipole moment derived from fluorescence and calculated quantum chemically for the FC geometry. Some of the possible factors involved have been given by Rechthaler et al.[12] and are discussed below together with some additional possible reasons.

We want to emphasize that these points all assume the validity of model 1; i.e., the solute can be described as a point dipole in a continuous surrounding with a certain polarizability generating a reaction field.

In the last section, we will discuss the consequences of model 2 (breakdown of the Onsager assumptions).

*(a) Vectorial Character of the Dipole Moment.* It is possible that the dipole moments of ground and excited state are not oriented in parallel but they could be oriented including an angle near to perpendicularity as discussed by Rechthaler et al.[12] Our calculations on DCB and DMDCB do not support this interpretation. The dipole moments all point along the long molecular axis, and the angular change from ground to excited state is 4° or smaller.

*(b) Absorbing and Emitting States Differ.* The main absorption transition could be to a state different from $S_1$, where fluorescence occurs. Then, the dipole moments derived from absorption and emission solvatochromy should of course differ. Our calculations show that $S_1$ is allowed and is the only absorbing state in this region because $S_2$ is 0.5 eV higher in energy, and this explanation can likewise be ruled out.

*(c) Enhancement of the Dipole Moment through Excited State Relaxation.* It could be envisaged that the structural changes occurring during the excited state relaxation enhance the value of the dipole moment considerably. A possible relaxation pathway is the shortening of double bonds and the lengthening of single bonds, together with a quinoid distortion of the benzene rings. We tested this possibility by excited state optimization (Table 3) and found that the bond length changes calculated do not lead to a significant increase of the excited state dipole moment. To enhance the quinoid character, we even shortened the central bonds of benzene to 1.35 Å and lengthened the adjacent bonds of the excited state optimized geometry to 1.45 Å (extreme quinoid geometry). For this rigid geometry, the dipole moment did not increase but even showed a slight decrease to 14.3 D.

A further relaxation possibility is especially interesting. This concerns the twisting of bonds, connected to the formation of twisted intramolecular charge transfer (TICT) states.[22] Such states have been described in the literature of donor−acceptor stilbenes.[26,33] On the other hand, our recent comparative study of the photophysical properties of DCB and DMDCB[28] indicates that the radiative rate constant/transition dipole moment is not small as would be expected from an emissive TICT state.[22] Moreover, there was no reduction of $k_f$ for the sterically hindered compound DMDCB. Both these observations led to the conclusion that an emissive TICT state is absent in DCB and DMDCB. Our calculation in the gas phase[28] indicate, that a relaxation to a TICT state is not spontaneous (i.e., without barrier) in $S_1$ (for details see section 4f). This behavior is parallel to that of related donor−acceptor biphenyl derivatives:[41−43] Dimethylamino-cyano-biphenyl does not form a TICT state in polar solvents, this occurs only when sterical hindrance (similar to that in DMDCB) is introduced. The experimental evidence is then a strong reduction of the radiative rate constant[41,42] (which is absent for DMDCB). This experimental behavior is also correctly reflected in qualitative terms: The excited state potentials change in polar solvents in a way that the unhindered biphenyl retains a minimum at the planar geometry, but the potential for the hindered derivative changes to a single minimum at 90°, and the excited state energy for the equilibrium geometry is significantly larger. Such a behavior is not found for DMDCB; i.e., the solvation energy that decreases the $S_{TICT}-S_1$ energy difference from the gas-phase value to acetonitrile (for DCB, this energy difference is 1.5 eV in the gas phase and 0.6 eV in acetonitrile)[28] is not sufficient to lower the TICT state below the less polar $S_1$ state even for DMDCB, and therefore the radiative rate constants are solvent independent for both compounds.[28]

*(d) Solvatochromic Fluorescence Shifts Induced by Changes of the Relative Size of the FC-Factors of the Emissive State.* The mixed solvent experiment (Figure 3.) excludes that solvent polarity dependent changes of the FC factors can enhance the fluorescence solvatochromy as apparent source.

*(e) Anomalously Large Polarizability of the Emissive State.* Polar solvents could enhance the dipole moment of the emissive state to an anomalously large degree. We tested this by performing calculations in a solvent surrounding. We took Zerner's[44] calculation on DMABN (using the ZINDO/S method) as a reference and compared to our calculation on DMABN (using the AM1/COSMO method[45]); we found that the relative increase of the dipole moment from cyclohexane to acetonitrile is comparable (15−18% with both methods). Table 5 shows our results for DCS and DCB. It can be seen that in both cases the allowed state is $S_1$, and its dipole moment increases from hexane to acetonitrile by 10% (DCS) and 5% (DCB) only. Moreover, increased solvent polarity slightly decreases the oscillator strength. These results show that excited state polarizability effects are even weaker here than in the well-studied case of DMABN.[22]

*(f) Ground State Structural Polarizability.* A further possibility can be envisaged in ground state structural polarizability effects. As Table 4 shows for DMDCB, the more twisted geometry at $\alpha = 45°$ shifts the absorption spectrum to the blue. If polar solvents induce a more twisted $S_0$ geometry (which can be called a structural polarizability), then the absorption red shift deriving from the solvatochromy of the highly polar $S_1$ state will be

partially or fully compensated by the blue shift due to the structural polarizability. This factor would allow us to understand the observed absence of absorption solvatochromy as an artifact resulting from compensation of opposing effects. In fact, the blue shift induced in DMDCB by 45° twist (0.33 eV) is more than sufficient to compensate the red shift of absorption from hexane to acetonitrile (0.2 eV) estimated on the basis of the calculated FC dipole moment. On the other hand, this explanation is not likely here, because the ground state dipole moment decreases with increasing twist angle (Table 4), and more polar solvents should therefore lead to a preferential population of the more planar geometries.

Summarizing the various points discussed within the assumptions of model 1, we can conclude that neither of the points considered allows us to understand the observation of a very small solvatochromic slope in absorption and a very large solvatochromic slope in emission for the molecules considered.

*(g) Local Solute−Solvent Interactions and Breakdown of the Onsager Point-Dipole Approximation.* Finally, we will discuss model 2 and assume the breakdown of the Onsager assumptions and therefore eqs 3 and 4. In this model, a very extended dipolar molecule possessing strongly polar local sites (e.g., partially charged end groups) could interact locally with the surrounding polar solvent molecules and by this way optimize the solute−solvent interaction beyond the value determined by the wave function that is perturbed only by the Onsager reaction field. This will then lead, in polar solvents, to solute dipole moments that are larger than expected from the Onsager model and also from the COSMO calculations, which assume a continuum solvent. This is equivalent to postulate a solute polarizability that is much larger than that found from the calculations in Table 5. Then the basis for the explanation of the strongly different solvatochromic slopes in absorption and emission is given by the local solute−solvent effects, which can only be effective on the time scale of the solvent structural relaxation, but not yet on the time scale of the absorption.

Table 6 and Scheme 4 (see Supporting Information) show the comparison of the solvatochromic slopes for absorption and emission and the derived experimental dipole moments for many members of the styrene, stilbene, and larger diphenylpolyene families. The analysis uses the two basic solvatochromic equations in a way that does not necessitate the use of ground state dipole moments from other sources. Purely experimental ground and excited state dipole moments can then be derived and compared to the calculated ground state dipole moment. As can be seen in Table 6, the anomalous effect consists mainly in the underrating of the experimental versus the calculated dipole moment of the ground state. In this comparison the groups of styrenes and the group of larger molecules (stilbenes and diphenylpolyenes) behave differently. In the styrene group, $\mu_g$ calculated corresponds well to $\mu_g$ experimental, but in the stilbenes and higher polyenes, $\mu_g$ experimental is much smaller than $\mu_g$ calculated. We think that this effect is not linked to the individual nature of the acceptor, because nitriles behave similarly as nitro and ester compounds and even (dimethylamino)stilbene (DS) without additional acceptor substituent is anomalous. Therefore the extended delocalization is suggested to be the source of the anomaly. In the very large systems, it may be possible that the electronic density is polarized by the polar solvent beyond the value expected from Onsager theory, because the charge distribution is so extended that the Onsager point dipole approximation is no longer valid. The polarization may also be increased by local interactions between the substituents and the solvent. A deeper understanding of these effects needs additional investigations including many more model compounds.

## 5. Conclusion

The solvatochromic behavior of the absorption and emission of a donor−acceptor diphenylpolyene is compared to the behavior of other diphenylpolyenes and to a series of styrenes. Whereas the diphenylpolyenes have an abnormal behavior where the absorption solvatochromy is nearly absent but that of the fluorescence is large, this is not the case for the styrenes. For the diphenylpolyenes, the observed dipole moments for FC and equilibrated $S_1$ states differ strongly. This cannot be explained on the basis of the quantum-chemically derived excited state properties including polarizability effects and neither by the solvatochromic equations based on the Onsager theory.

**Supporting Information Available:** Comparison of the solvatochromic slopes for absorption and emission and the derived experimental dipole moments for many members of the styrene, stilbene and larger diphenylpolyene families.This material is available free of charge via the Internet at http://pubs.acs.org.

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